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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Dibenzoate Esters of Aliphatic Diols and process for their preparation

We, UNION CARBIDE CORPORATION, (formerly known as Union Carbide and Carbon Corporation), of 30, East 42nd Street, New York, State of New York, United States of America, a corporation organised under the laws of the State of New York, United States of America, (assignee of GORDON MURRAY GOODALE, EDWARD JAMES MILLS, JR., THOMAS ROBERT MILLER and JAMES JOHN FASNACHT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing dibenzoate esters of aliphatic diols by reacting butyl benzoate with an aliphatic diol containing four to nine carbon atoms and having no tertiary hydroxyl groups. A tertiary hydroxyl group is one which is attached to a tertiary carbon atom.

Among the compounds which may be prepared in accordance with the present invention are the dibenzoate esters of aliphatic diols having an oxygen interrupted carbon chain, such as diethylene glycol dibenzoate, dipropylene glycol dibenzoate, and polyalkylene glycol dibenzoates and the dibenzoate esters of straight and branched chain aliphatic diols having an uninterrupted carbon chain, such as 2-ethyl-1,3-hexanediol; 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol; 2,5-hexanediol; 3-methyl-1,5-pentanediol; 2-ethyl-2-butyl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; 2,2-diethyl-1,3-propanediol; 2-methyl-1,5-pentanediol; 2-ethyl-3-methyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol; 2,4-diethyl-1,5-pentanediol and 1,5-pentanediol.

Dibenzoate esters of aliphatic diols of the class described above are useful as plasticizers for vinyl resins. Dipropylene glycol dibenzoate is particularly valuable as a plasticizer for polyvinyl chloride resins.

We have discovered that the dibenzoate esters of aliphatic diols which contain from 4 to 9 carbon atoms and which containing no tertiary hydroxyl group can be prepared by reacting one molecular proportion of one of the above described aliphatic diols with 2.5 molecular proportions of butyl benzoate in the presence of an alkaline catalyst. The reaction can be conducted at a temperature of from 100° C. to 250° C., and preferably from 150° C. to 180° C., for a period of from 10 hours to 30 hours. Although the reaction can be conducted at a pressure of from 0.1 mm. Hg to 200 mm. Hg, it is preferably conducted at a pressure of from 2 mm. Hg to 100 mm. Hg. Suitable catalysts for the reaction comprise alkali metal and alkaline earth metal oxides, hydroxides, alkoxides, carbonates and borates. Preferred catalysts are the alkaline earth metal oxides. Calcium oxide is a particularly suitable catalyst because of its good catalytic activity, low cost and ease of handling. Catalyst concentrations can vary from 0.06 per cent by weight to 1.4 per cent by weight but are preferably between 0.1 per cent by weight and 1.0 per cent by weight. By operating at a temperature in the range of from 158° C. to 180° C. with a catalyst concentration of 0.1 per cent by weight, excellent results are obtained, particularly in the production of dipropylene glycol dibenzoate. As the reaction proceeds, butanol is removed by distillation, followed by a mid-fraction, usually containing butanol and butyl benzoate and a third fraction of butyl benzoate. The pure dibenzoate ester of the aliphatic diol can be isolated from the residue by distillation or by filtration.

The following examples are illustrative:—

EXAMPLE I.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) of refined butyl benzoate and 2414 grams (18.0

mols) of dipropylene glycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 180—194° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 198° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a goose-neck head and an external nitrogen ebullator. The stripping operation was conducted at a temperature of 182° C. at less than 1.0 mm. Hg. The kettle residue was then treated with a decolorizing material, filtered, and recovered.

A yield of 81.7 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 86.4 per cent. The refined dipropylene glycol dibenzoate had a purity by saponification of 99.8 per cent, an acidity (as benzoic acid) of 0.02 per cent, a diol content of 0.69 per cent and the following physical properties:—

Refractive index at 20° C. - -	1.5288
Specific gravity (20/20° C.) -	1.1255
Color (based on Pt-Co scale)	35

EXAMPLE II.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) of refined butyl benzoate and 2414 grams (18.0 mols) of dipropylene glycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—187° C. The kettle temperature was then reduced slightly, the pressure was reduced to 80 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 187° C. The contents of the reaction kettle were cooled, mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping operation was carried out at a temperature of 210° C. and a pressure of 1.5 mm. Hg. The kettle residue was then treated with magnesol, filtered and recovered.

A yield of 82.6 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 87.3 per cent. The refined dipropylene glycol dibenzoate had a purity by saponification of 99.9 per cent, an acidity (as benzoic acid) of 0.06 per cent, a diol content of 0.72 per cent and a color (based on Pt-Co scale) of 35.

EXAMPLE III.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mols) of dipropylene glycol. Then 23 grams (0.5 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. After most of the excess butyl benzoate had been collected, the pressure was reduced to 0.5 mm. Hg and the temperature of the kettle was raised as rapidly as possible to around 205—207° C. The desired dipropylene glycol dibenzoate was then collected as distillate.

A yield of 86.1 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 78.8 per cent. The refined dipropylene glycol dibenzoate had a purity (by saponification) of 99.9 per cent, an acidity (as benzoic acid) of 0.05 per cent, a diol content of 0.22 per cent and the following physical properties:—

Refractive index at 20° C. - -	1.5297
Specific gravity (20/20° C.) - -	1.1236
Color (based on Gardner scale)	2.5
Boiling range - - - - - -	190—195° C. at 0.5 mm. Hg.

EXAMPLE IV.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mols) of dipropylene glycol. Then 4 grams (0.1 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 180° C. After most of the excess butyl benzoate had been collected, the pressure was reduced to 2.0 mm. Hg, and the temperature of the kettle was raised as rapidly as possible to around 215—220° C. The desired ester was then collected as distillate.

A yield of 81.2 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 90.2 per cent. The refined dipropylene glycol dibenzoate had a purity (by saponification) of 99.9 per cent, an acidity (as benzoic acid) of 0.17 per cent, a diol content of 0.19 per cent and the following physical properties:—

Refractive index at 20° C.	1.5287
Specific gravity (20/20° C.)	1.1224
Color (based on Pt-Co scale)	65
Boiling range	210—216° C. at 2 mm. Hg.

EXAMPLE V.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 1782 grams (4.0 mols) of refined butyl benzoate and 537 grams (10.0 mols) of dipropylene glycol. Then 1.26 grams (0.06 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The distillation of dipropylene glycol dibenzoate was carried out at a kettle temperature of 212° C. and a pressure above 1.0 mm. Hg.

A yield of 58.1 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 74.0 per cent. The refined dipropylene glycol dibenzoate had a purity (by saponification) of 98.5 per cent, an acidity (as benzoic acid) of 0.03 per cent., a diol content of 1.50 per cent and the following physical properties:—

Refractive index at 20° C.	1.5282
Specific gravity (20/20° C.)	1.1230
Color (based on Pt-Co scale)	35
Boiling range	200—204° C. at 1 mm. Hg.

EXAMPLE VI

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2228 grams (12.5 mols) of refined butyl benzoate and 531 grams (5.0 mols) of diethylene glycol. Then 2.76 grams (0.1 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The distillation of diethylene glycol dibenzoate was

carried out at a temperature of 210—220° C. and a pressure above 1.0 mm. Hg.

A yield of 73.7 per cent of diethylene glycol dibenzoate (based on diethylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 76.2 per cent. The refined diethylene glycol dibenzoate had a purity (by saponification) of 98.9 per cent, an acidity (as benzoic acid) of 0.07 per cent, a diol content of 1.0 per cent and the following physical properties:—

Refractive index at 20° C.	1.5438
Specific gravity (20/20° C.)	1.1746
Color (based on Pt-Co scale)	80
Boiling range	200—214° C. at 1 mm. Hg.

EXAMPLE VII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mols) of refined butyl benzoate and 731 grams (5.0 mols) of 2-ethyl-1,3-hexanediol. Then 33 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 198° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg. and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 200° C. After most of the excess butyl benzoate had been collected a stripping operation was carried out for ten minutes at a temperature of 220° C. and a pressure of 1.5 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 88.4 per cent of 2-ethyl-1,3-hexanediol dibenzoate (based on 2-ethyl-1,3-hexanediol) was obtained, with an efficiency (based on butyl benzoate) of 84.0 per cent. The refined 2-ethyl-1,3-hexanediol dibenzoate had a purity (by saponification) of 99.4 per cent, an acidity (as benzoic acid) of 0.14 per cent, a diol content of 0.2 per cent and the following physical properties:—

Specific gravity (20/20° C.)	1.0801
Color (based on Gardner scale)	5

EXAMPLE VIII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mols) of refined butyl benzoate and 731 grams (5.0 mols) of 2-ethyl-1,3-hexanediol. Then 30 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 196° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 200° C. The contents of the reaction kettle were cooled to around 130° C. mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping operation was carried out at 192° C. and 1 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 75.0 per cent of 2-ethyl-1,3-hexanediol dibenzoate (based on 2-ethyl-1,3-hexanediol) was obtained, with an efficiency (based on butyl benzoate) of 77.5 per cent. The refined 2-ethyl-1,3-hexanediol dibenzoate had a purity (by saponification) of 99.0 per cent, an acidity (as benzoic acid) of 0.18 per cent, a diol content of 0.52 per cent and the following physical properties:—

Refractive index at 20° C.	1.5317
Specific gravity (20/20° C.)	1.0814
Color (based on Gardner scale)	4

EXAMPLE IX

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 1068 grams (5.99 mols) of refined butyl benzoate and 441 grams (2.5 mols) of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol. Then 15 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then

distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate was carried out at a temperature of 232° C. and a pressure of 1.5 mm. Hg.

A yield of 83.1 per cent of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate (based on 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 79.0 per cent. The refined 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate had a purity (by saponification) of 99.8 per cent an acidity (as benzoic acid) of 0.14 per cent, essentially no diol content and the following physical properties:—

Refractive index at 20° C.	1.5310
Specific gravity (20/20° C.)	1.1003
Color (based on Pt-Co scale)	25
Boiling point	225° C. at 1.5 mm. Hg.

EXAMPLE X

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 446 grams (2.5 mols) of refined butyl benzoate and 160 grams (1.0 mols) of 2,4-diethyl-1,5-pentanediol. Then 5 grams of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—189° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of 2,4-diethyl-1,5-pentanediol dibenzoate was carried out at a temperature of 254° C. and a pressure of 4.0 mm. Hg.

A yield of 36.9 per cent of 2,4-diethyl-1,5-pentanediol dibenzoate (based on 2,4-diethyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 44.8 per cent. The refined 2,4-diethyl-1,5-pentanediol dibenzoate had a purity (by saponification) of 99.6 per cent, an acidity (as benzoic acid) of 0.62 per cent, a diol content of 0.04 per cent and the following physical properties:—

Refractive index at 20° C.	1.5322
Specific gravity (20/20° C.)	1.0775
Color (based on Pt-Co scale)	30
Boiling point	206° C. at 1 mm. Hg.

EXAMPLE XI

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45 mols) of refined butyl benzoate and 2125 grams (18 mols) of 3-methyl-1,5-pentanediol. Then 101 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190—200° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 190° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping operation was carried out at a kettle temperature of 180—189° C. and a pressure of 2 to 4 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 85.3 per cent of 3-methyl-1,5-pentanediol dibenzoate (based on 3-methyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 86.6 per cent. The refined 3-methyl-1,5-pentanediol dibenzoate had a purity (by saponification) of 100.2 per cent, an acidity (as benzoic acid) of 0.01 per cent, essentially no diol content and the following physical properties;—

Refractive index at 20° C.	1.5378
Specific gravity (20/20° C.)	1.1103
Color (based on Pt-Co scale)	70
Boiling range	186—192° C. at 1 mm. Hg.
Freezing point	—33.4° C.

EXAMPLE XII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with stainless steel protruded packing and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 1338 grams (7.5 mols) of refined butyl benzoate and 480 grams (3.0 mols) of 2-ethyl-2-butyl-1,3-propanediol. Then 18.2 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 90 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 140° C. The kettle temperature was then reduced slightly, the pressure was reduced to 75 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 160° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of 2-ethyl-2-butyl-1,3-propanediol dibenzoate was carried out at a temperature of 237—267° C. and a pressure of 1.5 mm. Hg.

A yield of 64.7 per cent of 2-ethyl-2-butyl-1,3-propanediol dibenzoate (based on 2-ethyl-2-butyl-1,3-propanediol) was obtained, with an efficiency (based on butyl benzoate) of 87.4 per cent. The refined 2-ethyl-2-butyl-1,3-propanediol dibenzoate had a purity (by saponification) of 100.8 per cent, an acidity (as benzoic acid) of 0.02 per cent, diol content of 0.39 per cent and the following physical properties:—

Refractive index at 20° C.	1.5327
Specific gravity (20/20° C.)	1.0778
Color (based on Pt-Co scale)	20
Boiling range	236° C. at 1.5 mm. Hg.

EXAMPLE XIII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with stainless steel protruded packing and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 200 grams (1.5 mols) of 2-methyl-2-propyl-1,3-propanediol and 670 grams (3.75 mols) of refined butyl benzoate. Then 9 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature rose to 156° C. The kettle temperature was reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 170° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 249—252° C. and a pressure of 2.0 mm. Hg.

A yield of 48.2 per cent of 2-methyl-2-propyl-1,3-propanediol dibenzoate (based on 2-methyl-2-propyl-1,3-propanediol) was obtained. The refined 2-methyl-2-propyl-1,3-propanediol dibenzoate had a purity of 101.8 (by saponification), essentially no acidity and diol content and the following physical properties:—

Refractive index at 20° C.	1.5367
Specific gravity (20/20° C.)	1.1003
Color (based on Pt-Co scale)	20
Boiling range	214° C. at 2 mm. Hg.
Freezing point	—5.6° C.

EXAMPLE XIV

In a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with stainless steel protruded saddles, and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 670 grams (3.75 mols) of refined butyl benzoate and 200 grams (1.5 mols) of 2,2-diethyl-1,3-propanediol. Then 9 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was

heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 165° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 184° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 200° C. and a pressure of 2.0 mm. Hg.

A yield of 42.9 per cent of 2,2-diethyl-1,3-propanediol dibenzoate (based on 2,2-diethyl-1,3-propandiol) was obtained, with an efficiency (based on butyl benzoate) of 51.1 per cent. The refined 2,2-diethyl-1,3-propanediol dibenzoate had a purity of 101.2 per cent (by saponification), essentially no acidity, a diol content of 0.34 per cent, and the following physical properties:—

Refractive index at 20° C.	1.5402
Specific gravity (20/20° C.)	1.1097
Color (based on Pt-Co scale)	18
Boiling range	211—214° C. at 2 mm. Hg.
Freezing point	—5° C.

EXAMPLE XV

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 802 grams (4.5 mols) of refined butyl benzoate and 236 grams (2.0 mols) of 2-methyl-1,5-pentanediol. Then 10 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 171° C. The kettle temperature was reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 195° C. The contents of the reactor kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 200 to 210° C. at 2.0 mm. Hg.

A yield of 88.3 per cent of 2-methyl-1,5-pentanediol dibenzoate (based on 2-methyl-1,5-pentanediol) was obtained, with an efficiency of 88.8 (based on butyl benzoate). The refined 2-methyl-1,5-pentanediol dibenzoate had a purity of 99.8 per cent (by saponification) an acidity (as benzoic acid) of 0.12, essentially no diol content and the following physical properties:—

Refractive index at 20° C.	1.5379
Specific gravity (20/20° C.)	1.1045
Color (based on Pt-Co scale)	18
Boiling range	203—204° C. at 2 mm. Hg.
Freezing point	—3.8° C.

EXAMPLE XVI

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with stainless steel protruded packing and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 850 grams (4.77 mols) of refined butyl benzoate and 264 grams (2.0 mols) of 2-ethyl-1,5-pentanediol. Then 11 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 154° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 187° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 218—221° C. and a pressure of 1.5 mm. Hg.

A yield of 89.8 per cent of 2-ethyl-1,5-pentanediol dibenzoate (based on 2-ethyl-1,5-pentanediol) was obtained with an efficiency (based on butyl benzoate) of 91.4 per cent. The

refined 2-ethyl-1,5-pentanediol dibenzoate had a purity (by saponification) of 99.9 per cent, an acidity (as benzoic acid) of 0.13 per cent, and a diol content of 0.69 per cent, and the following physical properties:—

Refractive index at 20° C.	1.5356
Specific gravity (20/20° C.)	1.0945
Color (based on Pt-Co scale)	20
Boiling range	215—218° C. at 1.5 mm. Hg.
Freezing point	—35° C.

EXAMPLE XVII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 620 grams (3.48 mols) of refined butyl benzoate and 200 grams (1.31 mols) of 2-ethyl-3-methyl-1,5-pentanediol. Then 8 grams (1.0 per cent by weight of the kettle charge) of lime (technical grade calcium oxide) were added and the reaction mixture was heated to 110° C. and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190° C. The kettle temperature was then reduced slightly, the pressure was reduced, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure was required to facilitate maintenance of the kettle temperature below 212° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temperature of 217—222° C. and a pressure of 2.0 mm. Hg.

A yield of 86.0 per cent of 2-ethyl-3-methyl-1,5-pentanediol dibenzoate (based on 2-ethyl-3-methyl-1,5-pentanediol) was obtained, with an efficiency (based on butyl benzoate) of 79.7 per cent. The refined 2-ethyl-3-methyl-1,5-pentanediol dibenzoate had a purity of 98.7 per cent (by saponification), an acidity (as benzoic acid) of 0.12 per cent, a diol content of 0.41 per cent and the following physical properties:—

Refractive index at 20° C.	1.5362
Specific gravity (20/20° C.)	1.0945
Color (based on Pt-Co scale)	18
Boiling range	210—218° C. at 2 mm. Hg.
Freezing point	—17.2° C.

WHAT WE CLAIM IS:—

1. Process for preparing dibenzoate esters of aliphatic diols which comprises reacting butyl benzoate with an aliphatic diol containing 4 to 9 carbon atoms and having no tertiary hydroxyl groups as hereinbefore defined.

2. Process as claimed in Claim 1 in which one molecular proportion of the aliphatic diol is reacted with 2.5 molecular proportions of butyl benzoate.

3. A process as claimed in Claim 1 or 2 in which the reaction is effected in the presence of an alkaline catalyst.

4. Process as claimed in Claim 3 in which the alkaline catalyst is an alkali metal or alkaline earth metal oxide, hydroxide, alkoxide, carbonate or borate.

5. Process as claimed in Claim 4 in which the alkaline earth metal oxide is calcium oxide.

6. Process as claimed in Claim 3, 4 or 5 in which the catalyst concentration is between 0.1% and 1.0% by weight.

7. Process as claimed in any of Claims 1 to 6 in which the reaction is effected at a temperature of from 150° C. to 180° C.

8. Process as claimed in any of Claims 1 to 7 in which the reaction is effected at a pressure of from 2 mm. of mercury to 100 mm. of mercury.

9. Process as claimed in any of Claims 1 to 8 in which the aliphatic diol is dipropylene glycol.

10. The dibenzoate ester of 2-ethyl-1,3-hexane diol.

11. The dibenzoate ester of 2-methyl-1,5-pentanediol.

12. The dibenzoate ester of 2-ethyl-1,5-pentanediol.

13. The dibenzoate ester of 2-ethyl-3-methyl-1,5-pentanediol.

14. The dibenzoate ester of 2,4-diethyl-1,5-pentanediol.

15. The dibenzoate ester of 2-ethyl-2-butyl-1,3-propanodiol.

16. The dibenzoate ester of 2-methyl-2-propyl-1,3-propanediol.

17. Process for preparing dibenzoate esters of aliphatic diols substantially as herein described with reference to and as illustrated in the foregoing examples.

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